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SURFACE PROTONIC CONDUCTION IN POROUS OXIDES*

Recent years have brought renewed interest in the well-known phenomenon of protonic conduction in water adsorbed on surfaces and hence enhanced conductivity in porous materials. Beyond the effect of reducing the resistance of insulators and use in humidity sensors, there is interest in potential application as electrolyte in electrochemical cells. This is inherently troubled by the need for high relative humidities (low temperatures and/or high steam pressures) unless the surfaces are doped with e.g. hygroscopic phosphoric or sulphuric acids. It is increasingly acknowledged how adsorbed water and surface protonic conduction play roles also in many other processes, like heterogeneous catalysis, solid-state electrode kinetics and photoelectrochemistry.

A first layer of water chemisorbs on hard surfaces at relatively high temperatures and gives rise to modest conduction of dissociated but fairly strongly bonded protons. As temperature decreases and relative humidity (RH) increases, an additional layer of water is physisorbed by strong hydrogen bonds, displaying an ice-like structure. The chemisorbed and ice-like physisorbed layers exhibit Grotthuss-type proton (H^+) conduction [1]. Above 60 % RH the water layer passes approximately 1 nm in thickness and becomes liquid-like, with lower activation energy for proton mobility and strongly increasing conductivity by vehicle mechanisms involving H_3O^+ or OH^- ions depending on the acid-base properties of the materials surface.

On oxide surfaces, cations act as adsorption sites for the chemisorbed water molecules, which partially dissociate protons to the surface oxide ions, creating proton hopping sites on both adsorbed and surface oxide ions.

The addition of physisorbed water molecules gives additional possibilities for protons to jump, and as the layer gets thick enough to become liquid-like, the mobili-

ty of the vehicular species increases. Equally important is probably that the spread of charge carriers (normally envisaged as protons, at least for acidic oxides) drives the dissociation reaction into charge separation and a double layer space charge structure with enhanced charge carrier concentrations.

A simple brick model of grains and pores is introduced to make first approximation estimates of surface protonic conduction of porous materials.

Intersecting grain boundaries may invert the space charge and give rise to high resistances [2].

It has recently been reported that also dry hydrogen gas adsorbs and dissociates on insulating oxides and gives rise to surface protonic conduction, which has been shown to affect catalytic properties in experiments with a dispersed catalyst and an electric field and surface protonic current [3].

References

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